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Titania nanostructure arrays from lithographically defined templates

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We report the fabrication of TiO_2 nanostructures with lithographically defined templates. Interferomeric-lithography was used to define soft templates (polymer posts), and a sol-gel solution was deposited on a patterned surface. In the final step, calcination was employed to form uniform low aspect-ratio crystalline nonclose-packed TiO_2 nanotube arrays over a large area. Similarly, nanotree arrays and parallel nanotunnels were prepared as well. The position and morphology of TiO_2 nanostructures were well controlled. These TiO_2 nanostructures have a potential technological importance in clean energy, biosensor, and drug release. © *2010 American Institute of Physics*. [doi:10.1063/1.3521462]

Since self-ordering of TiO_2 nanotubes was discovered using titanium anodization,[1–3] intense research has been carried out to optimize fabrication approaches and find applications.[4] Beyond the vertical TiO_2 nanotubes achieved by a simple one-step electrochemical self-assembly process, other types of TiO_2 nanostructures with different fabrication approaches and templates are also of interest; to date, relatively simple preparation methods based on a sol-gel process have been pursued. For example, crystalline titania nanorings were fabricated with monolayer particle templates and sol-gel deposition.[5,6] Complex crystalline titania structures were prepared with bio-organic templates (e.g., butterfly wing scales) and the use of layer-by-layer sol-gel deposition.[7] The resulting synthesized replicas had a rutile structure using dopant sol-gel solution and calcination at relatively low temperatures of ~450 °C. In addition, physical deposition techniques such as pulsed laser deposition were developed to fabricate hierarchical TiO_2 nanostructures by combining colloidal monolayers.[8]

TiO_2 is a useful functional material due to its wide application in the field of photocatalysis,[8,9] dye-sensitized solar cells,[10] lithium-ion batteries,[11] and superhydrophobic/superhydrophilic materials.[8,12] Well-controlled morphologies of titania nanostructures are critical for these applications. Close-packed nanotube/nanoring arrays of titania have been intensively studied, but other nanoscale morphologies of TiO_2 nanostructures such as nonclose-packed, low aspect-ratio titania nanostructures could provide compelling uses in morphology-dependent applications.

Even though interferometric lithography (IL) has been used to generate templates for the fabrication of simple two-dimensional (2D) metal nanowires and nanorings with electrochemical deposition,[13] it is still a challenge to use IL to produce templates for the fabrication of TiO_2 nanostructure arrays.

Here, we present a simple approach for fabricating position-controlled TiO_2 nanostructure arrays by sol-gel deposition using photoresist patterns as templates. The photoresist pattern templates were fabricated with IL. After sintering at 600 °C, the crystal structure of the ordered TiO_2 nanostructures changes from amorphous to anatase, while maintaining the original morphology.

IL is a facile, inexpensive, large area, lithographic method for the fabrication of periodic nanostructures and functional materials.[14] The patterns produced with IL are often used for further fabrication[15,16] in applications such as optics,[17,18] biosensors,[19] and nanofluidic devices.[20] Here, we used IL to produce one-dimensional (1D) and 2D photoresist (PR) patterns with periodicities in the range of 300 nm to 2 μm. Smaller periodicity ranges, up to 90 nm, are readily accessible with immersion approaches.[21]

Figure 1 shows the scanning electron microscopy (SEM) images of 2D PR patterns and the corresponding prepared TiO_2 nanostructures. The PR posts were fabricated with IL

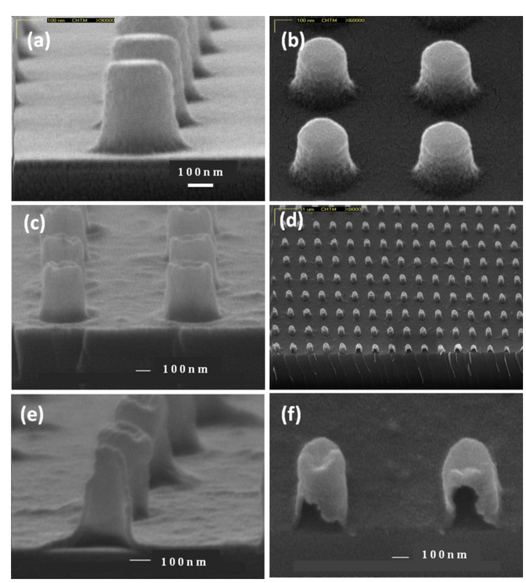

FIG. 1. (Color online) SEM images: [(a) and (b)] photoresist patterns; [(c) and (d)] nanodrum; [(e) and (f)] nanodrum with breaking during cleavage, showing the hollow structure; side view in the left column, and tilted 45° view in the right column.

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using positive PR. The periodic PR posts are on a square array using double IL exposures with 90° rotation between the two exposures [Figs. 1(a) and 1(b)]. IL has the advantages of uniform patterns over large areas, and flexibility of pattern morphologies (line/space duty cycle, periodicity, and variations, e.g., hexagonal, in the array patterns by changing the rotation angle between exposures).[22] With spin-coating deposition of a sol-gel solution and calcination, 2D nanostructures of TiO_2 were obtained, as shown in Figs. 1(c)–1(f). Importantly, the hollow structure of the individual shapes is obvious from the observations of broken TiO_2 nanostructures [Figs. 1(e) and 1(f)]. The dimensions of the TiO_2 nanostructures are slightly smaller than those of the PR post due to the shrinkage of TiO_2 nanostructures during the processing of spin-coating and calcinations. The shrinkage of resultant TiO_2 nanostructures compared to the original PR templates are caused by both the partial dissolution of PR templates upon coating with the sol-gel solution and formation of TiO_2 nanostructures in calcination processing. The top surface of TiO_2 nanostructures is uneven in the images. The TiO_2 nanostructures with 870 nm periodicity have an ~220 nm diameter, are 400 nm high, and 20 nm thick.

The calcination was performed at 600 °C for 3 h. The temperature is high enough to totally burn out the PR patterns. In our preliminary experiments, we investigated the effects of changing the calcination temperatures on the morphology of the PR templates. The PR patterns [posts as shown in Figs. 1(a) and 1(b)] restructured into polymer lenses after 3 h of calcination at 450 °C for a bare PR patterned sample, while the PR patterns were totally vaporized after 3 h of calcination at 600 °C. The diffraction color of the periodic patterns on a PR patterned sample provided an easy method to verify the temperature effect. Therefore, we used calcination at 600 °C for 3 h in air to form the TiO_2 nanostructures.

Transmission electron microscopy (TEM) was used to examine further the morphology and crystallinity of the TiO_2 nanostructures. The TEM samples were prepared by scratching the as-prepared samples and capturing the TiO_2 fragments with a Cu TEM grid sample holder. Figure 2 shows both low-resolution and high-resolution TEM images. These images further confirm that TiO_2 nanostructures are hollow, closed-end short nanotubes. It is apparent that these TiO_2 nanostructures have relatively uniform sizes [Figs. 2(a) and 2(b)] with wide openings at the bottom. TEM images in Figs. 2(c)–2(e) exhibit three, two, and one TiO_2 nanostructures, respectively, from the side view, while the TEM image in Fig. 2(f) shows the top view of a TiO_2 nanostructure which appears to be ring shaped. These findings are consistent with the SEM observations. These images indicated that the titania sol-gel coating uniform is conformal to the polymer surface.

The calcination at 600 °C for 3 h both vaporizes the polymer templates and converts the coating into nanocrystalline titania. The nonclose-packed, short titania nanotube arrays were retained after firing at 600 °C. High-resolution TEM (HRTEM) images revealed that the titania was mainly in the anatase phase [Fig. 2(g)].[23] With further calcination or modification of sol-gel solution by introducing tin (IV) isopropoxide as a rutile-promoting dopant, the TiO_2 nanostructures will be converted to the rutile TiO_2 crystal structure.[8] With electrostatic layer-by-layer deposition of titania nanoparticles using polymer templates defined by IL, continuous anatase titania wires or dots would be achieved through calcinations at 500 °C for 2 h.[24]

We also investigated other sol-gel deposition methods and extended the spin-coating method to other morphologies of PR patterns such as 1D structures (Fig. 3). A sandwich

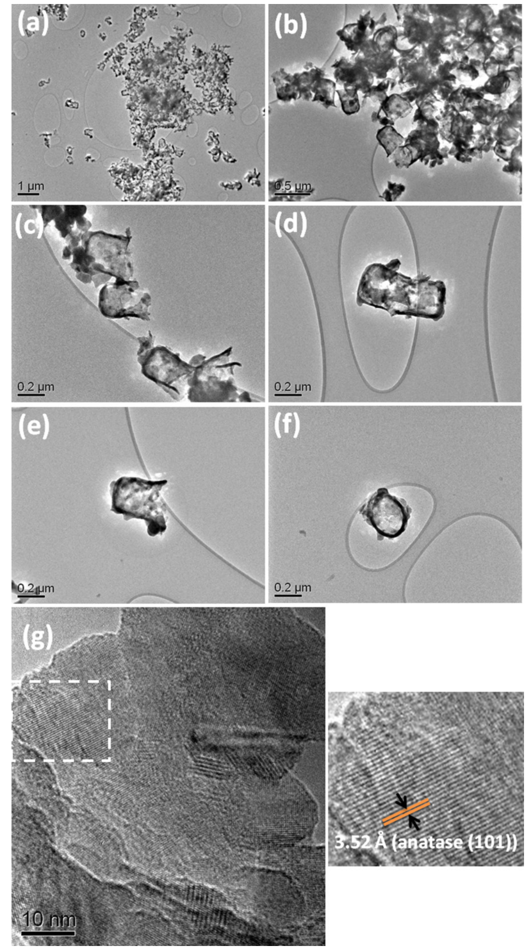

FIG. 2. (Color online) TEM images: [(a) and (b)] TiO_2 nanostructrures; (c) three TiO_2 nanostructrures; (d) two TiO_2 nanostructrures; (e) single TiO_2 nanostructure; (f) top view of single TiO_2 nanostructure; (g) HRTEM showing anatase lattice, right one is a magnified image and a white dashed square in left image.

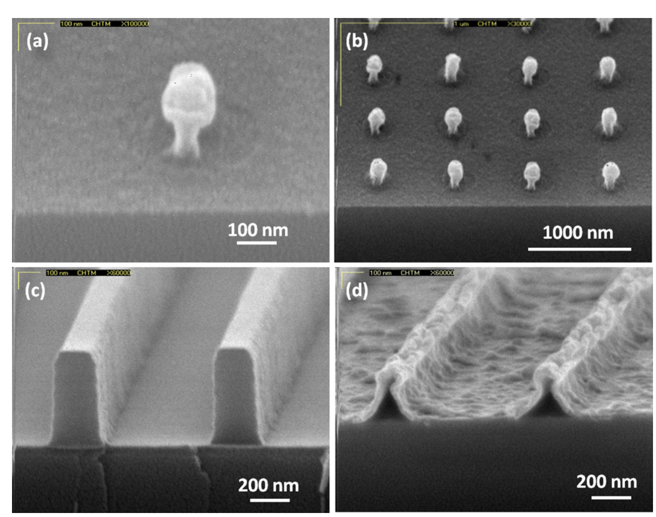

FIG. 3. (Color online) SEM images of TiO_2 nanostructures: [(a) and (b)] nanotrees; (c) 1D PR patterns; (d) nanochannels.

sol-gel method was used as well to apply the solution between two glass plates.[5] A different morphology of TiO_2 nanostructures was achieved on 2D PR post templates [Figs. 3(a) and 3(b)]. The TiO_2 nanostructure exhibited the shape of a nanotree with a slim trunk and a wide crown [Fig. 3(a)]. Even though the TiO_2 nanostructure arrays over the whole sample were obtained using this deposition approach, the morphology of nanotrees is not uniform [Fig. 3(b)]. The TiO_2 nanotree structures were caused by the partial dissolution of the PR patterns in titanium (IV) isopropoxide solution in this sandwich deposition method. In our preliminary experiments, after the samples with 2D PR patterns were immersed into an isopropanol solution for 2 h, the 2D PR posts were deformed.

One-dimensional PR walls were also employed to form 1D TiO_2 nanostructures using a spin-coating deposition method. Parallel TiO_2 nanotunnels were fabricated with 1D PR wall templates [Figs. 3(c) and 3(d)]. The nanotunnels have wide bottoms and uneven roofs (including some openings). Shrinkage of 1D TiO_2 structures was observed as well, especially in the height of the nanotunnels. The morphology (long parallel wall, narrow top surface, etc.) of 1D PR walls was attributed the formation of 1D TiO_2 nanotunnels, which have less fidelity to templates in spin-coating deposition and calcination processes. Compared to the previous work with IL-defined templates, sol-gel processing, and calcination,[25] we fabricated nanochannel structures instead of nanowires using our approach on a 1D template.

It is relatively easy to fabricate close-packed ultralong TiO_2 nanotube arrays with anodization and nanoring films with colloidal lithography. However, it is difficult to fabricate low aspect-ratio nanostructures with tailored morphologies.[26] Compared to conventional morphologies (nanotubes and nanorings), unique morphologies of low aspect-ratio nanotubes with nonclose-packed arrays, nanotree arrays, and parallel nanotunnels were fabricated with interference lithography using our methods. Moreover, a continuous flat sheet of TiO_2 between the structures appears to connect these structures. Combined with standard optical lithography, the corresponding devices are easy to fabricate on substrates with position-control of the TiO_2 nanostructures. In addition, this approach will be applicable to the fabrication of other kinds of inorganic hollow structures using related sol-gel solutions with IL-defined templates.[27]

In summary, various titania nanostructures were fabricated using lithographically defined polymer templates. The polymer templates including 1D and 2D patterns in a nanoscale were easily formed with interferometric lithography. The morphology of templates was easy to control in interference lithography step with the advantage of flexible control of the interferometic lithography pattern. With spin-coating deposition of sol-gel solution and subsequent hydrolysis step, uniform 2D closed-end low aspect-ratio nanotube arrays were prepared over large areas in nonclose-packed arrays. The crystalline phase of titania nanostructures could be controlled in the hydrolysis step. Furthermore, the nanotree and nanotunnel structures were fabricated as well with IL-defined templates. Compared to the previous research,[24,25] we can fabricate hollow TiO_2 nanostructures (short nanotubes and nanotunnels) instead of nanowires and nanoholes using our approach. These TiO_2 nanostructures have technological importance in clean energy,[28,29] biosensors,[30] and controlled drug release.[31]

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